



Plastic crystalline-semi crystalline polymer composite electrolyte based on non-woven poly(vinylidene fluoride-co-hexafluoropropylene) porous membranes for lithium ion batteries



Nageswaran Shubha^a, Raghavan Prasanth^{a,b}, Hng Huey Hoon^a, Madhavi Srinivasan^{a,b,*}

^a School of Materials Science and Engineering, Nanyang Technological University, Block N4.1, 50 Nanyang Avenue, Singapore 639798, Singapore

^b Energy Research Institute @ NTU (ERI@N), Research Techno Plaza, 50 Nanyang Drive, Singapore 637553

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ABSTRACT

The advantageous properties of both solid soft matter electrolytes and polymer gel electrolytes (PGEs) are combined to develop a electrospun polymer composite electrolyte (PCE) for lithium ion batteries; based on addition of butanedinitrile (BDN, the plastic crystal) to poly(vinylidene fluoride-co-hexafluoropropylene) {P(VdF-co-HFP)} (semi crystalline polymer). Polymer composite electrolytes are prepared by activating the fibrous membrane with 1 M LiPF₆ in EC/DEC. The electrochemical characterization shows that the addition of BDN significantly improves the ionic conductivity of composite electrolytes even at lower temperatures due to the active role played by BDN in ion conduction. Also the compatibility of the polymer composite electrolyte with lithium electrode improves by incorporation of BDN. Galvanostatic cycling test demonstrates the suitability of these polymer composite electrolytes for lithium ion batteries in both Li/PCE/LiFePO₄ (half cell) and LTO/PCE/LiFePO₄ (full cell) configurations. The addition of BDN improves the charge discharge performance and cycling stability of the polymer composite electrolytes.

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1. Introduction

Lithium ion batteries (LIBs) have been widely used as power sources for portable devices such as laptops, mobile phones, cameras etc. Recently they are being considered for application in electric vehicles/hybrid electric vehicles (EV/HEV) and stationary energy storage devices to make them eco-friendly by enabling zero emission and slowing down global warming. When lithium ion batteries scale up from portable power sources to electric vehicles, one of the main factors that needs to be considered is its safety due to the flammability and leakage of the organic electrolytes generally used in LIBs. Many researchers have reported the use of solid polymer electrolytes (SPEs) in LIBs, which improve safety through reduction of vapor pressure and elimination of liquid electrolyte. Unfortunately the room temperature ionic conductivity (10^{-4} S cm⁻¹), transference number and electrochemical performance of these electrolytes are poor. In this scenario, to utilize the beneficial characteristics of both (liquid electrolyte and SPE) systems, hybrid electrolyte concept called polymer gel electrolytes (PGEs) which provides lighter and safer batteries with longer shelf

life, leak proof construction and easy fabrication into desired shape and size [1–3] was explored. PGEs reported have ionic conductivity of the order 10^{-3} S cm⁻¹, electrochemical stability window exceeding 4.5 V and good compatibility with lithium electrodes [3]. However, from the practical point of view the dimensional stability of these electrolytes are not enough for easy handling and thereby it is not an ideal mechanical substrate for LIBs. PGEs are prepared by activating the host polymer matrix (generally a porous polymer membrane) by immersing it in a liquid electrolyte. Upon gelling these electrolytes predominantly show three phases: solid polymer matrix, gelled polymer phase and absorbed liquid electrolyte encapsulated in the pores and cavities of the host membrane [4]. Conductivity of the PGE is mainly influenced by the gelled phase and liquid phase, while the solid phase contributes towards mechanical strength. The ability of the membrane to absorb electrolyte greatly depends on the porosity, pore structure and pore distribution of the membrane. Thus a highly porous membrane exhibits high ionic conductivity, but at the same time, increase in porosity may lead to a decrease in mechanical strength. Therefore increasing ionic conductivity without compromising the mechanical strength has been the main focus of researchers working on PGEs. The addition of ceramic fillers to the host matrix [3,5,6], blending of polymers [7,8], structural modification and/or cross linking [9] of polymers are reported to improve ionic conductivity, without reducing mechanical integrity of PGEs.

* Corresponding author. Tel.: +65 67904606; fax: +65 67909081.
E-mail address: madhavi@ntu.edu.sg (M. Srinivasan).

More recently plastic solid soft matter electrolytes have been reported as a new class of electrolyte materials for LIBs in which lithium salts are doped in to the matrices of plastic crystals to yield pliable materials. Plastic crystal solvent from pyrazolium imide family such as 5-methyl-5,6,7,8-tetrahydropyrazolo (1,2-a) pyridazin-4-ium trifluoromethanesulfonimide, *N,N*-pentamethylene pyrazolium bis(trifluoromethanesulfonyl imide), [10,11], *N,N'*-diethyl-1-3-methylpyrazolium bis(trifluoromethanesulfonyl imide) or butanedinitrile (BDN) doped with lithium bis-trifluoromethanesulfonyl imide (LiTFSI) [Li(CF₃SO₂)₂N], LiBF₄, LiPF₆ and LiCF₃SO₃ salt [12,13] were reported. The studies showed that ionic conductivity and electrochemical properties of BDN is better compared to pyrazolium imide based electrolytes [14,15]. BDN is a highly polar plastic crystal, has high dielectric constant ($\epsilon=55$) [14] and good solvating ability (lithium salt dissociation capability) [15]. It is also reported as a versatile ion promoter [15]. BDN-salt electrolytes conduct only in the plastic phase (between -38 and 58 °C) due to presence of trans-gauche isomerism involving rotation of molecules about the central C–C bond. The trans isomer has been proposed as an impurity phase which results in enhancement of lattice defects and lowering of activation energy for ionic conduction, thereby directly affecting the ionic conductivity [16]. Unlike ceramic fillers, which increase the conductivity of PGEs by affecting the Lewis acid base interaction between the filler and the host matrix [3,5,6], BDN actively participates in ion conduction mechanism and is directly involved in increasing ionic conductivity, because of the presence of active ion hopping centers [15,17,18]. In the present study, we are reporting a plastic crystalline-semi crystalline polymer composite electrolyte (PCE), which combines the advantageous properties of both PGEs and plastic solid soft matter electrolytes. P(VdF-co-HFP) is used as the host polymer for preparing the polymer composite electrolyte. The composite membrane is prepared by electrospinning. The electrospun composite membrane acts as a highly porous sponge like material capable of holding large amounts of liquid electrolyte and BDN acts as plastic crystalline soft matter. P(VdF-co-HFP) is selected for this study, because of its high dielectric constant (~ 8.2) [4], excellent electrochemical properties, and affinity to the electrolyte owing to the presence of highly electronegative fluorine atom in its back bone [19]. Electrospinning is specifically adopted to prepare the porous membrane, to tailor easy ion conduction path for the movement of Li⁺ ions. In addition, the membrane properties such as membrane morphology, porosity, pore density and thickness can be controlled by changing the spinning parameters such as solution concentration, feed rate, bore size of the needle, applied spinning voltage, and distance between the collection drum and tip of the needle. The fully interconnected pore structure of electrospun membranes (ESMs) facilitates the easy penetration and absorption of large amounts of liquid electrolyte and the cobweb structure of the membrane formed by the stacking of micron-submicron fibers help to hold the absorbed electrolyte without/minimum electrolyte leakage (electrolyte retention), which makes them a good candidate as a host membrane for polymer composite electrolytes. The polymer matrix acts as the mechanical substrate and the plastic crystalline BDN enhances the transfer rate by offering active ion hopping centers for the lithium ions [18].

2. Experimental

2.1. Preparation of P(VdF-co-HFP)-BDN composite membranes

P(VdF-co-HFP) used in the present study was Kynar Flex 2801 ($M_w=4.77 \times 10^5$, VdF/HFP ratio: 88/12, Elf Atochem) and BDN

(99% purity, Aldrich, $M_w=80.09$). P(VdF-co-HFP) vacuum dried at 60 °C for 12 h and BDN was vacuum dried at room temperature for 48 h before use. The solvents acetone and *N,N*-dimethylacetamide (DMAc) (HPLC grade, Aldrich) were used as received. A uniform solution of 16 wt% P(VdF-co-HFP) in a mixed solvent of acetone/DMAc (7:3, w/w) was prepared by magnetic stirring for 24 h at room temperature. Varying content of BDN was added to the solution and stirred for another 6 h to get a uniform solution. The BDN content was varied from 0–9% by weight of P(VdF-co-HFP). The resulting P(VdF-co-HFP)-BDN solution was kept undisturbed for 15 min to get a bubble free clear solution. Sufficient quantity of the solution at a constant flow rate was fed to the steel needle having bore size of 0.6 mm using a syringe infusion/withdrawal pump (KD Scientific, Model-210). The tip of the needle was connected to high voltage source and the solution was directly electrospun onto a grounded, aluminum drum covered with thin aluminum foil, rotating at specified speed at ambient atmosphere. The essential electrospinning parameters were as follows: applied voltage ~ 16 –20 kV (depending on the viscosity of the solution), working distance from collector to tip of the needle ~ 20 cm, bore size of the needle 0.6 mm, solution feed rate 15 ml h⁻¹ and collection drum rotation speed 150 rpm. The as spun fibers in the form of free standing non-woven membrane of average thickness ~ 150 μ m with sufficient mechanical strength were collected and dried at 60 °C for 12 h to remove any traces of solvent. Before activation of the membranes, they were dried in the antechamber of the glove box under vacuum at room temperature for 48 h. The membranes were designated as ESM-01, ESM-02, ESM-03 and ESM-04 respectively for electrospun membrane based on P(VdF-co-HFP) with BDN content (wt%) 0, 3, 6 and 9 to highlight their respective composition.

2.2. Characterization of P(VdF-co-HFP)-BDN composite membranes

Surface morphology of the membranes was examined with high resolution field-emission scanning electron microscope (FE-SEM: Jeol JSM7600F) at an accelerating voltage of 15 kV. The samples were mounted on metal stubs using conductive double-sided tape, and a thin layer of platinum was sputter coated on the sample using Jeol JFC-1200 prior to scanning. Average fiber diameter (AFD) was estimated from the micrograph taken in high magnification. About 300 fibers were estimated. Crystallinity of the composite were evaluated by differential scanning calorimetry (DSC: 2950, TA Instruments) thermal scans from 0 °C to 350 °C under N₂ atmosphere at a heating rate of 10 °C min⁻¹. Porosity (*P*) was determined by immersing the dry membrane in *n*-butanol for 1 h [5]. The membrane was weighed before and after immersion in *n*-butanol to measure the mass of *n*-butanol absorbed. Following relation was used to calculate *P*:

$$P(\%) = \frac{M_{\text{BuOH}}/\rho_{\text{BuOH}}}{M_{\text{BuOH}}/\rho_{\text{BuOH}} + M_m/\rho_p} \times 100$$

where M_m is the mass of the dry membrane, M_{BuOH} is the mass of *n*-butanol absorbed by the membrane, ρ_{BuOH} and ρ_p are the densities of *n*-butanol and polymer, respectively.

Polymer composite electrolyte based on P(VdF-co-HFP)-BDN were prepared by dropping optimized amount of the liquid electrolyte, 1 M LiPF₆ in EC/DEC (1:1, w/w) (Danvecon Technologies Pvt. Ltd) on a circular piece of membrane (area ~ 2 cm²). This procedure for activation of membranes was specifically adopted, because it was suspected that BDN may dissolve in the liquid electrolyte. Therefore while activating the membrane with liquid electrolyte even if BDN dissolves/leach out from the membrane, it remains in the liquid phase of the polymer composite electrolyte. The capacity of the membrane to absorb liquid electrolyte (electrolyte uptake) was measured by soaking the composite membrane in the

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